Differential Scanning Calorimetric Study of Solid State Amorphization and Crystallization in Zr/Co and Zr/Ni Multilayers

Differential Scanning Calorimetric Study of Solid State Amorphization and Crystallization in Zr/Co and Zr/Ni Multilayers*

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Synopsis

The processes of solid state amorphization (SSA) and subsequent crystallization in Zr/Co and Zr/Ni multilayered thin films have been studied by differential scanning calorimetry (DSC). The thermodynamic values, i.e., the enthalpy change ΔH_a and the activation energy E_a for amorphization as well as the enthalpy change ΔH_x and the activation energy E_x for crystallization have been evaluated from the DSC experiments. These values were compared with those of the corresponding rapidly quenched amorphous alloys. The activation energies E_a, calculated by the modified Ozawa method, are 150 and 132 kJmol^{-1} for Zr/Co and Zr/Ni multilayers respectively. These values are equivalent to the previously reported activation energy of diffusion of Co or Ni in the rapidly quenched amorphous Zr-Co or Zr-Ni alloys.

I. Introduction

Amorphous alloys can be primarily prepared by rapid quenching from the liquid or the vapor phases. Recently, a novel technique for the preparation of amorphous alloys, called solid-state amorphization (SSA), has been developed by Schwarz and Johnson.[1] They have demonstrated SSA by isothermal annealing of Au/La polycrystalline multilayer films. This phenomenon has subsequently been found in other systems including Zr/Co[2] and Zr/Ni.[3-8] The process and the mechanism of the SSA have been investigated by the microscopic methods, for example, Rutherford back scattering[8] and cross sectional TEM observation.[2]

It has been proposed that the necessary conditions for the SSA

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are as follows.[1,9] The first is thermodynamically downhill process in which free energy is greatly lowered. The second is the absence of the sufficient atomic mobility of one of two species and relatively substantial mobility of another. The third is the reaction under the sufficiently lower temperature than the crystallization temperature. However, the values related to the kinetics and the thermodynamics for SSA have scarcely been obtained. The purpose of the present work is to measure the enthalpy change, the activation energy and the temperature range of SSA and subsequent crystallization in multilayer films, and to compare these values with those of the amorphous alloys prepared by rapid quenching. In this work we examine the solid state amorphization and subsequent crystallization using a differential scanning calorimeter (DSC).

II. Experimental

The Zr and TM (TM=Co, Ni) sublayers were deposited on to a substrate on a water cooled table by alternative sputtering of the targets. Then codeposition was completely avoided. The sputter deposition chamber was evacuated to base pressure less than $4x10^{-5}$Pa by liquid-nitrogen-trapped diffusion pump. The deposition was performed at a power density of 2.6Wcm^{-2} in an argon (99.9999%) atmosphere at a pressure of 2Pa. The ratio of the layer thickness of Zr to Co and Zr to Ni were 2.11 to 1 and 2.13 to 1 respectively, which gave an overall atomic composition ratio of Zr to TM (TM=Co, Ni) of 1 to 1. The modulation length λ was 20nm and the total film thickness was 600nm for both samples. Free-standing multilayer films for DSC measurements were prepared by first coating glass with polymer. The films were removed from the glass substrates by dissolving the polymer in organic solvent.

The $Zr_{50}Co_{50}$ ingot was prepared by arc melting a mixture of pure Zr and Co metals in an argon (99.9995%) atmosphere. The amorphous $Zr_{50}Co_{50}$ ribbons were produced by the single-roller melt-spinning technique in an argon atmosphere (99.9995%).

The multilayer thin films and rapidly quenched amorphous alloys were thermally analyzed by the Seiko DSC220 differential scanning calorimeter (DSC) at the heating rate from 5 to 80Kmin^{-1} in an argon gas (99.9995%) flow atmosphere. The first scan was followed immediately by the second scan. The second scan was subtracted from the first one to elucidate phase transformations. Some of the samples were heated to the given temperatures and then were rapidly cooled by a forced convection of argon gas to examine its structure by X-ray

diffraction (XRD). The XRD measurement was performed by the X-ray diffractometer (θ-2θ scan) using monochromated CuKα radiation.

III. Results

1. DSC measurement

Figure 1 shows the DSC curve of Zr/Co multilayers heated at the rate of 40Kmin^{-1}. The ordinate represents the heat flow that corresponds to the rate of solid state reactions. Two exothermic peaks are clearly observed. In order to see the nature of the peaks, XRD measurements were carried out for the sample heated to the distinct stages. Figure 2 shows the XRD patterns of the as-prepared Zr/Co multilayers, samples heated to the distinct stages and a sample isothermally annealed at 500K for 100ks. The as-prepared sample shows strong textures, i.e. the (001) plane of Zr layers with the hcp structure and the (111) plane of Co layers with the fcc structure are parallel to the substrate. The formation of metastable fcc αCo phase by the sputtering method has been previously reported in Zr/Co[2] and Cu/Co[10] multilayers, although the equilibrium fcc αCo phase is stable above 695K. The sample heated to 640K by DSC, which is well below the crystallization temperature, shows the great decrease of the intensities of the Bragg Peaks and the appearance of the broad peak, indicating the formation of the amorphous phase. Although we could not obtain a single phase amorphous alloy by DSC, we obtained the fully amorphized sample by the isothermal annealing

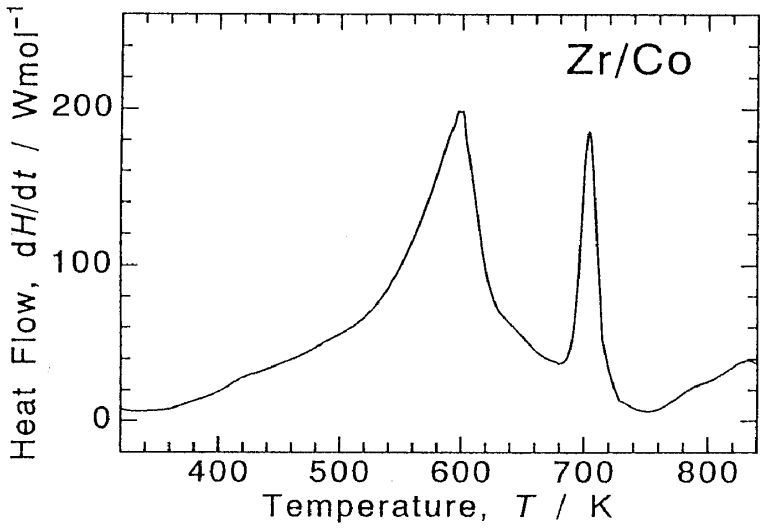

Fig. 1. The differential scanning calorimetry (DSC) curve of sputtered Zr/Co multilayers heated at 40Kmin^{-1}. The average composition is $Zr_{50}Co_{50}$ and a modulation wavelength is 20nm.

at 500K for 100ks as seen in Fig.2. From these XRD experiments, we can see that the first broad exothermic peak from 350 to 680K is due to the solid state amorphization (centered at temperature T_a=599K). This broad DSC curve means that the growth of amorphous phase is carried over a wide temperature range. The intermetallic compound ZrCo was observed in the sample heated up to 840K by DSC, although small amount of unreacted Co and zirconium oxides were detected as seen in Fig.2. Therefore, we can conclude that the second sharp exothermic peak corresponds to polymorphous crystallization (centered at T=704K). The crystallization occurred drastically in comparison with SSA. The enthalpy changes for amorphization ΔH_a and crystallization ΔH_x are derived from the reasonably separated area of each peak. These values are averaged for all heating rates. The calorimetric values obtained for multilayers and the rapidly quenched amorphous $Zr_{50}Co_{50}$ alloy are summarized in Table I. The details of these values are discussed in the next section.

Figure 3 shows the DSC curve of Zr/Ni multilayers heated at the rate of 40Kmin^{-1}. This curve is very similar to that of ZrCo. The XRD patterns of Zr/Ni multilayers heated to the distinct stages in DSC are shown in Fig.4. The hcp Zr (001) plane and the fcc Ni (111) plane of the sublayers are parallel to the substrate in as-prepared state. The

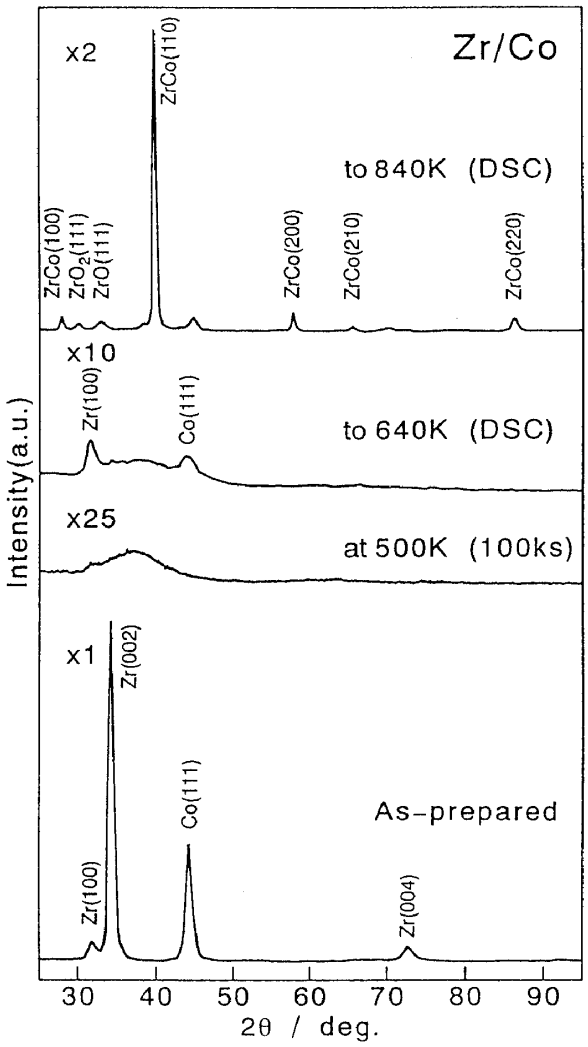

Fig. 2. The X-ray diffraction patterns (CuKα) for Zr/Co multilayers heated to the distinct stages in DSC and cooled to the room temperature subsequently and that isothermally annealed for 100ks at 500K.

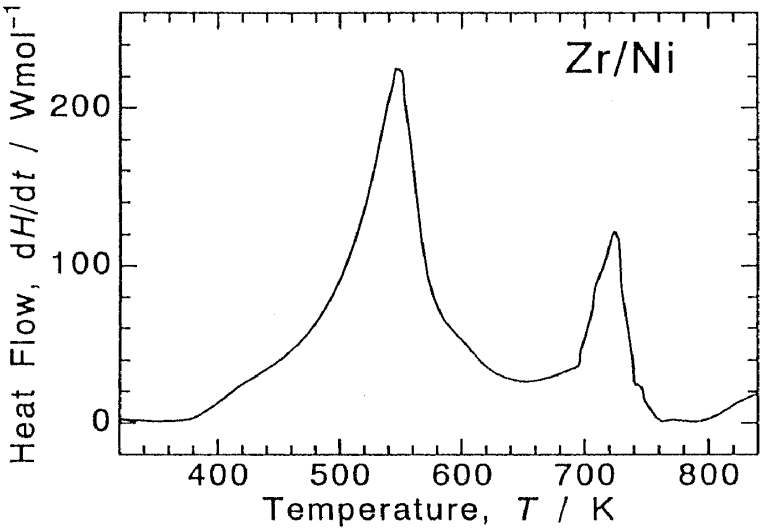

Fig. 3. The differential scanning calorimetry (DSC) curve of sputtered Zr/Ni multilayers heated at 40Kmin^{-1}. The average composition is $Zr_{50}Ni_{50}$ and a modulation wavelength is 20nm.

Table I. The results of DSC measurements for amorphization and crystallization of Zr/Co and Zr/Ni multilayers and the corresponding rapidly quenched amorphous alloys, ΔH_a: the formation enthalpy of amorphous alloys, E_a: the activation energy of amorphization, T_p: the peak temperature of SSA, ΔH_x: the enthalpy change for crystallization, E_x: the activation energy of crystallization, T_x: the crystallization temperature.

		Zr/Co multilayer ($Zr_{50}Co_{50}$)	Rapid quench amorphous ($Zr_{50}Co_{50}$)	Zr/Ni multilayer ($Zr_{50}Ni_{50}$)	Rapid quench amorphous ($Zr_{55}Ni_{45}$)
Amorphization	ΔH_a (kJmol^{-1})	-29	-36[a]	-30	-34[b]
	E_a (kJmol^{-1})	150[c]	147[d] (Diffusion)	132[c]	140[e] (Diffusion)
	T_p (K)	599 (40Kmin^{-1})	——	548 (40Kmin^{-1})	——
Crystallization	ΔH_x (kJmol^{-1})	-4.6	-7.2	-5.3	-5.1[f]
	E_x (kJmol^{-1})	227[g]	297[g]	296[g]	299[f,g]
	T_x (K)	704 (40Kmin^{-1})	740 (40Kmin^{-1})	713 (20Kmin^{-1})	710[f] (20Kmin^{-1})

a Reference 15 : the estimated value based on the eq.(2)
b Reference 16 and 17 : the estimated value based on the eq.(2)
c the estimated value based on the modified Ozawa method
d ^{57}Co diffusion in amorphous $Zr_{89}Co_{11}$ Ref.13
e ^{63}Ni diffusion in amorphous $Zr_{50}Ni_{50}$ Ref.14
f Reference 17
g the estimated value based on the Kissnger method

sample heated to 610K shows the decrease of the intensities of the Bragg Peaks and the appearance of the broad peak, indicating the formation of the amorphous phase. Then, the first exothermic peak from 380 to 650K is due to SSA (centered at temperature T=548K, which was about 50K lower than Zr/Co). The intermetallic compound ZrNi was formed in the sample heated up to 840K as seen in Fig.4. Therefore, we can conclude that the second exothermic peak corresponds to polymorphous crystallization (centered at T=725K). The calorimetric data of Zr/Ni multilayers are summarized in Table I. The details of these values are discussed in the next section.

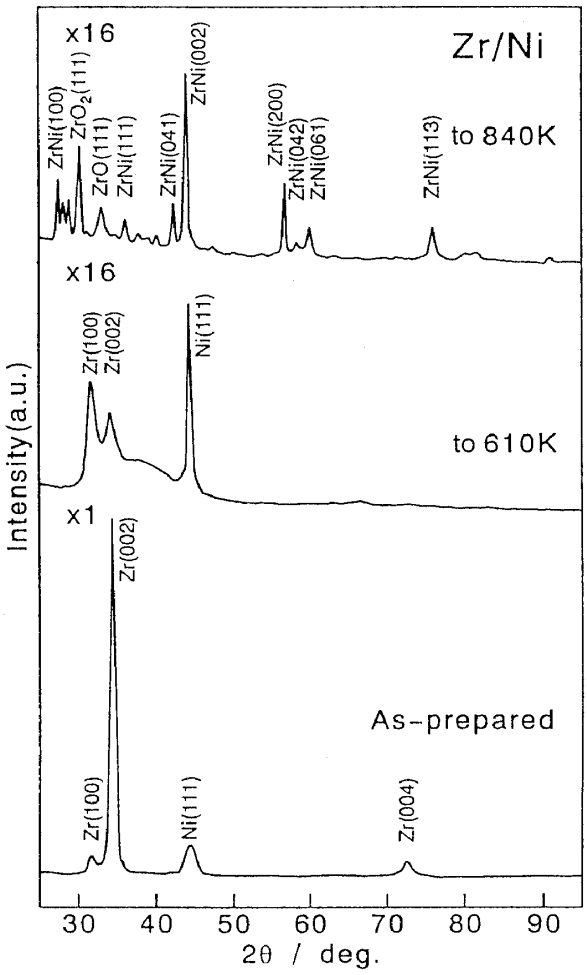

Fig. 4. The X-ray diffraction patterns (CuKα) for Zr/Ni multilayers heated to the distinct stages in DSC and cooled to the room temperature subsequently.

2. DSC data analysis of amorphization

Some analysis methods have been proposed to calculate the activation energy from the DSC experiment. They are derived from the relation between the heating rate (α) and the temperature (T) at which the rate of reaction reaches a specific value. By this analysis the systematic error is weakened. The following two methods have been generally used for DSC experiment of amorphous alloy. The Kissinger method[11] has been widely used as a standard for the estimation of the apparent activation energy of the crystallization of amorphous alloys. On the other hand, the modified Ozawa method[12] reflects the reaction mechanism in itself. Then, we used this to calculate the activation energy E_a of solid state amorphization. The equation is expressed as follows,

$$\ln \alpha = -\frac{mE}{nRT_p} - \ln[\ln(1-x)] + \text{Const}, \qquad (1)$$

where R is the gas constant, x is the rate of reaction, n and m are the numerical factors depending on the reaction mechanism. Since SSA of Zr/Ni and Zr/Co evolve by the progress of the amorphous layer between different metal layers[2], the number of the amorphous layer is constant till the end of the reaction. These reaction mechanisms correspond to the bulk nucleation with the constant number of nuclei and the one-dimensional growth for the modified Ozawa plot (n=1, m=1). We used the peak temperature of DSC curves as the maximum temperature (T_p) where the rate of reaction reaches its maximum. The actual plots are shown in Fig. 5. The correlation is quite well. The derived values of the activation energies are shown in Table I. The details of these values are discussed in the next section.

IV. Discussion

First, we discuss the analysis method to obtain the activation energy of the SSA from the DSC data. Highmore et al.[6,7] calculated the activation energy of SSA by the fitting of the DSC curves to the differential equation about the amorphous phase growth rate. The equation is derived from the one-dimensional diffusion equation. This method has the advantage that the activation energy is calculated by the DSC measurement at only one constant heating rate. However, we can not measure the sample temperature itself, but the sample holder temperature by DSC. It is a result of the heat resistance between the sample and the temperature sensor. Therefore the DSC heat flow (dH/dt) does not exactly correspond to the differential equation, especially for non-isothermal measurement. Furthermore, DSC curves are affected by the deviation of modulation wave length.[6] Therefore, the activation

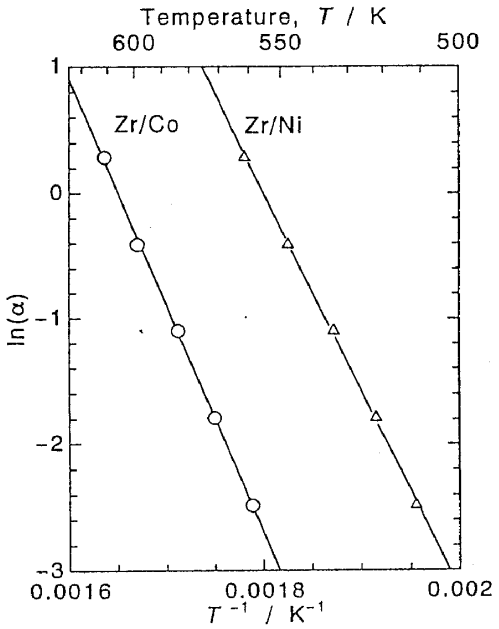

Fig.5. The modified Ozawa plots for solid state amorphization (SSA) of Zr/Co and Zr/Ni multilyers.

energy derived by this fitting method will contain systematic error.

As can been seen from Table I, the activation energies of SSA (E_a), obtained from the modified Ozawa method, are in good agreement with those of the early transition metal diffusion in amorphous alloys, namely ^{57}Co in $Zr_{89}Co_{11}$[13] and ^{63}Ni in $Zr_{50}Ni_{50}$.[14] This agreement gives a kinetic evidence that SSA is progressed by the diffusion control mechanism in the amorphous layer. Thus, the modified Ozawa method is convenient and suitable to obtain the activation energy for SSA.

Next we discuss about the enthalpy change for amorhization in multilayered films and the conventional rapid quenching. The formation enthalpy of amorphous alloy (ΔH_a) for SSA is directly derived from the integration of DSC exothermic peak. On the other hand, ΔH_a for the rapidly quenched amorphous alloy is estimated from the enthalpy change ΔH_x for crystallization by using the following relation.

$$\Delta H_c = \Delta H_a + \Delta H_x, \qquad (2)$$

where ΔH_c is the formation enthalpy of the intermetallic compound[15,16] with same composition as amorphous alloy. This equation contains the assumption that the specific heat of alloy does not depend on its structure and can be applied only for the case of polymorphous crystallization. Table I shows the values of ΔH_a obtained from the DSC data of SSA and those calculated from the rapidly quenched sample data[17] by eq.(2). As seen in Table I, the former is smaller than the latter. This may be due to the partial formation of amorphous alloys by the collision of high energy particles during sputtering deposition. The formation enthalpy of amorphous alloy is much greater than the enthalpy change for subsequent crystallization. This implies that structural configurations are not so different between the intermetallic compounds and the amorphous alloys in comparison with that of elemental metals.

The Kissinger method[11] was used to obtain apparent activation energies for crystallization. As can be seen from Table I, both the enthalpy change and the activation energy for crystallization of the amorphous ZrNi alloy prepared by SSA are very similar to those prepared by rapid quenching. This suggests that the structures of both alloys are similar. On the contrary, in the case of ZrCo the enthalpy change for crystallization of the amorphous alloy prepared by SSA is smaller than that of the rapidly quenched sample. Furthermore the lower crystallization temperature (T_x) is measured for the former. This may be due to the non-reacted Co layer between amorphous

layers, as can be seen from Fig.3, because the inclusions in the amorphous alloys act generally as the preferential nucleation site. The disagreement of the apparent activation energies of the crystallization between two amorphous alloys suggests the difference of the crystallization mechanism.

V. Conclusion

The reactions in Zr/Co and Zr/Ni multilayered films were examined by differential scanning calorimetry (DSC). The thermodynamic or kinetic values for solid state amorphization (SSA) and crystallization were obtained. The activation energies of SSA, which were calculated by modified Ozawa method, are comparable to the previously reported activation energies of diffusion of Co or Ni in the rapidly quenched amorphous Zr-Co or Zr-Ni alloys. This means that the DSC measurement and the modified Ozawa plot are the suitable method to study the activation energy for solid-state amorphization. Crystallization behaviors of amorphous ZrNi alloy prepared by SSA is very similar to that by rapid quenching, but not for amorphous ZrCo alloy.

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References

1) R.B.Schwarz and W.L.Johnson:Phys. Rev. Lett., **51** (1983) 415.
2) H.Shrdöer, K.Samwer and U.Köster: Phys. Rev. Let., **54** (1985) 197.
3) B.M.Clements, W.L.Johnson and R.B.Schwarz: J. Non-Cryst. Solids, **61-62** (1984) 817.
4) L.Schultz: *Proceedings of the 5th International Conference on Rapidly Quenched Metals, Wurzburg, 1984*, edited by S.Steeb and H.Warlimont (North-Holland, Amsterdam, 1985), p.1585.
5) E.J.Cotts, W.J.Meng and W.L.Johnson: Phys. Rev. Let., **57** (1986) 2295.
6) R.J.Highmore, R.E.Somekh, J.E.Evetts and A.L.Greer: J. Less-Common Met., **140** (1988) 353.
7) R.J.Highmore, J.E.Evetts, A.L.Greer and R.E.Somekh: Appl. Phys. Lett., **50** (1987) 566.

8) J.C.Barbour: Phys. Rev. Let., **55** (1985) 2872.
9) W.L.Johnson: Prog. Mater. Sci., **30** (1986) 81.
10) J.R.Dutcher, S.Lee, C.D.England, G.I.Stegeman and C.M.Falco: Mater. Sci. Eng., **A126** (1990) 13.
11) H.E.Kissinger: Anal. Chem., **29** (1957) 1702.
12) K.Matsusita, S.Sakka: Bull. Inst. Chem. Res., Kyoto Univ., **59** (1981) 159.
13) H.Mehrer and W.Dörner: Defect and Diffusion Forum, **66-69** (1989) 189.
14) K.Hoshino, R.S.Averback, H.Hahn and S.J.Rothman: Defect and Diffusion Forum, **59** (1988) 225.
15) P.A.Gomozov, Yu.V.Zasypalov and B.M.Mogtnov: Russ. J. Phys. Chem. **60** (1986) 1122.
16) M.P.Henaff, C.Colinet, A.Pasturel and K.H.J.Buschow: J. Appl. Phys., **56** (1984) 307.
17) C.G.Mckamy, D.M.Kroeger, D.S.Easton and J.O.Scarbrough: J. Mater. Sci., **21** (1986) 3893.